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Upgrading of hydrothermal liquefaction biocrudes from mono- and co-liquefaction of cow manure and wheat straw through hydrotreating and distillation

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ABSTRACT

Liquid hydrocarbons from agricultural wet wastes can serve as a strategy to greatly reduce CO_2 emissions. This study presents the upgrading via catalytic hydrotreatment of hydrothermal liquefaction (HTL) biocrudes derived from cow manure, wheat straw and their combined liquefaction (co-HTL). Four different temperatures were tested (340, 360, 380 and 400 °C) at constant hydrogen and biocrude flowrate. The co-HTL biocrude contained more recalcitrant nitrogen-containing molecules towards hydrotreatment, which caused decreased hydrogen consumption and overall lower quality of upgraded products. Generally, upgraded products were obtained with >80 wt% carbon yields based on biocrude input. Products of hydrotreatment at 400 °C were distilled into four cuts. Increased hydrotreatment temperature improved physicochemical properties of upgraded products, leading to generally higher yields of gasoline and kerosene through significant cracking of bottom residues. Bottom residues derived from single feedstock HTL biocrudes were totally miscible with fossil-derived vacuum gas oil at room temperature, while the co-HTL derived one required increased temperature for total solubility. We show that the co-HTL approach leads to a higher production of the diesel and bottom residue fractions. Overall, single feedstock HTL resulted in a carbon yield from biomass to upgraded oils of 34 and 38 % respectively for wheat straw and cow manure, while the co-HTL approach increased this value to 43 %. The combination of agribusiness waste for HTL processing is shown here to be an attractive solution for wet waste processing and carbon recovery towards advanced biofuels.

1. Introduction

Liquid hydrocarbons are commodities of upmost importance for the world's current economy, playing the role of energy carriers [1]. Today, such liquids are derived in almost its entirety from fossil reserves – namely crude oil, coal and natural gas – causing an increase in greenhouse gas concentration in earth's atmosphere by linearly converting carbon-based materials into its oxidized form (CO_2). As the natural process of converting CO_2 back to a fossil reserve requires several orders of magnitude longer time than their extraction and emission, the increase in concentration of CO_2 will not cease until fossil reserves usage becomes obsolete. The consequences of CO_2 build-up in the atmosphere are severe and the global climate crisis will further worsen if no action is taken towards a carbon neutral economy [2].

The aviation, shipping and heavy-duty transportation sectors are particularly impacted by its dependency on liquid fuels composed of hydrocarbons [3]. According to the International Energy Agency, out of the 121 EJ of energy used for transportation worldwide in 2019, 110 EJ came from fossil reserves, and only a small 4 EJ from biofuels [4]. Converting wet agricultural waste into liquid fuels could greatly alleviate greenhouse gas emissions by using photosynthetic-reduced carbon [5]. There is an estimated 39 EJ of energy globally in the form of agricultural crop straw available. If the whole crop waste is accounted, this number increases to 78 EJ [5]. That, combined with approximately 10 EJ of recoverable animal faeces [6,7] offer a great opportunity to alleviate fossil dependence in the transportation sector.

Several routes of conversion of these materials are available, however wet waste conversion into liquid hydrocarbons by hydrothermal

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liquefaction has been gaining attention, as it avoids energy-demanding drying processes and is able to convert otherwise wasted carbon into an intermediate oil product referred to as biocrude [8]. The combination of different agricultural wastes has been proven to be beneficial to biocrude production, which can also be beneficial regarding logistics by enlarging the amount of feedstock materials available locally [7].

When straw and manure are processes by HTL, these biocrude intermediate oils are composed of around 62–75 % carbon, 6–9 % hydrogen, 0–5 % nitrogen and 10–24 % oxygen (wet basis) and have a higher heating value (HHV) of 28–34 $MJ.kg^{-1}$ [7]. Biocrudes from lignocellulosic and agricultural waste are typically composed of phenolics, ketones, alcohols, heteroatom-containing aromatics, amines and other molecules [9,10]. Such oil has a high viscosity derived from its molecular composition, which combined with its low HHV compared to typical liquid fuels makes upgrading a necessary step before final use of fuel, fuel blendstock or refinery feedstock.

The first efforts in catalytic upgrading via hydrotreatment of HTL biocrudes were reported in the early 80′s and are summarized in a publication by Elliott (2007) [11], using both model compounds and HTL biocrudes from the Albany Biomass Liquefaction Pilot Plant. Cobalt-Molybdenum (CoMo) and Nickel-Molybdenum (NiMo) sulfided catalysts supported on alumina were identified as promising approaches for deoxygenation of these types of oil, and given their classic use in fossil refining processes for denitrogenation [12], these catalysts are until today the preferred choice for bio-oil upgrading via hydrotreatment. Since then, several reports have used similar catalysts for upgrading of HTL biocrudes in batch and continuous processing from algae [13–18], lignocellulosic materials [18,19], sewage sludge [18,20] and pyrolysis bio-oils [21–25]. While fast pyrolysis bio-oils have been reported to deactivate NiMo catalysts when processed via hydrotreating [23], recently, HTL biocrude hydrotreating using a two-stage catalyst bed of CoMo and NiMo with temperature gradient over the reactor was shown to have an extended lifetime for upgrading of wet waste biocrude up to 1500 h of steady-state operation [26].

The aim of the study is to investigate the effect of different biocrude compositions on hydrotreatment and final distillate quality. Specifically, this study aims at elucidating the effects of biocrudes derived from synergistic co-HTL versus their respective individual feedstock HTL biocrudes on hydrotreatment. The biocrude's production process and synergistic effects were reported elsewhere [7], and the current work investigates the influence of temperature on the hydrotreatment of three different biocrudes. These biocrudes were produced in a continuous HTL pilot plant at relevant scale [27,28], from wheat straw, cow manure and a third one from the optimized mixing ratio of both feedstock materials. Physicochemical properties of the upgraded oil products from different hydrotreatment temperatures are evaluated and discussed. Biocrudes were hydrotreated in a continuous apparatus, mimicking expected conditions in large scale operations. Products from the most severe hydrotreatment temperature (400 °C) were distilled and the composition of distillate cuts are discussed regarding their possible application as fossil fuel replacements. By evaluating the quality of upgraded oils and distillate cuts and estimating the biomass to biofuel carbon efficiency, we highlight here the potential benefits and drawbacks of this approach to produce bio-based hydrocarbons.

2. Materials and methods

2.1. Hydrothermal liquefaction

Three separate HTL campaigns were conducted with wheat straw (hereafter referred to as straw), cow manure (hereafter referred to as manure) and an optimized mixture (1.1:1.0 Manure:Straw mix ratio) of both feedstock materials (hereafter referred to as co-HTL) in a continuous HTL pilot plant [27] located at Aarhus University's facilities in Foulum, Denmark. The HTL mixture ratio optimization is described elsewhere [7], together with other details about the continuous biocrude production, carbon and energy balances. In short, biocrude, carbon and energy yields were modelled based on batch HTL and the continuous HTL pilot plant was used in three campaigns, producing the three different biocrudes used in this study. Part of the biocrude product from HTL was then filtered using acetone as solvent (1:1 acetone to biocrude mixing by weight) using a 20 μm paper filter. The solvent was then evaporated in a rotary evaporator and around 2.5 kg of each biocrude was taken for each hydrotreatment experiment. Acetone residual concentration was determined to be lower than 0.5 wt% by GC/MS analysis.

2.2. Hydrotreatment of biocrudes

Catalytic hydrotreatment was carried out in a co-current, down flow, packed bed reactor with hydrogen (99.9 %) flowing at a rate of 45 $NL.h^{-1}$ and 80 bar of pressure. The catalyst packing was selected based in previous studies [26,29] which showed extended time on stream of a double-bed catalyst approach with temperature gradient in the first section of the reactor for upgrading of HTL biocrudes. In the current study, we also use a double-bed catalyst approach of crushed (590 to 1000 μm) CoMo (35 g of 2.8 wt% Co and 10.3 wt% Mo in Al_2O_3) and NiMo (50 g of 2.5 wt% Ni and 13.4 wt% Mo in Al_2O_3) commercial catalysts. The two catalyst zones were separated by a layer of 3 mm glass balls to better position the catalyst beds inside the reactor zones and allow accurate temperature control of the different beds. The simplified process flow diagram and reactor packing details are shown in Fig. S1.

Catalysts were sulfided *in situ* with 4.4 wt% dimethyl disulfide in hydrotreated gasoil flowing at a rate of 60 $g.h^{-1}$, with a hydrogen flow of 70 $NL.h^{-1}$, pressure of 40 bar and temperature ramped from ambient to 330 °C in the whole reactor at 15 $°C.min^{-1}$, holding the final temperature for a minimum of 4 h. After sulfiding, the catalysts' activity was stabilized for a minimum of 24 h running with straight run gas oil at 60 $g.h^{-1}$, hydrogen flow rate of 30 $NL.h^{-1}$, pressure of 40 bar and temperature of approximately 290 °C before biocrude was introduced.

The three biocrude upgrading campaigns were conducted using freshly *in-situ* sulfided catalysts with constant biocrude weight hourly space velocity (WHSV) of 0.7 h^{-1} for CoMo and 0.5 h^{-1} for NiMo (biocrude flow rate of 25 $g.h^{-1}$, translating to a hydrogen to oil mass ratio of 0.18). To adjust the sulfur content in straw biocrude, dimethyl disulfide was added to this biocrude, achieving the same concentration as in other feedstock materials. The CoMo zone was heated to around 150 °C in the intake and temperature rose up to around 340 °C by the end of the first bed due to the exothermic reactions and set point temperature in the following reactor section. Four different temperatures were tested for the NiMo bed, starting with the least severe (340 °C) and stepping up by 20 °C to the most severe condition (400 °C). At each temperature (340, 360 and 380 °C), sampling started after a minimum of 4 h stabilization and lasted for approximately 3 h. For the last temperature (400 °C) the sampling continued until the biocrude feedstock ran out and it was divided into two equal aliquots (hereafter referred to as 400I and 400II). Figure S2 A-C depicts the temperature, pressure and gas flows for all three campaigns. The reactor pressure drop during the entire time on stream did not exceed 1 bar in all experiments. Figure S3 A-C shows the reactor average temperature profiles for each temperature tested in all three campaigns, from which the reactor temperature average was calculated using the first 4 thermocouples of the NiMo zone. After collection, the hydrotreated products were separated into two phases, which are further referred to as aqueous and oil phases. Yield determination was conducted after product centrifugation to ensure complete phase separation.

2.3. Distillation of hydrotreated products and miscibility test

The oil phase of the three hydrotreated products – straw, manure and co-HTL – collected at 400 °C (both 400I and 400II) in each campaign were mixed and distilled in a batch distillation apparatus Fischer® Scientific with a SPALTROHR HMS 500 spiral column with 90

theoretical plates. Distillation cuts are labeled here as gasoline range (<150 °C), kerosene range (150–250 °C), diesel range (250–360 °C) and bottom residue (BR) (>360 °C). All distillations took place with reflux ratio of 1 and adequate pressures, avoiding cracking by limiting the temperature in the distillation flask to 250 °C. Kerosene and diesel were distilled under vacuum, while gasoline was distilled at atmospheric pressure.

Bottom residue fractions were tested individually for solubility in vacuum gas oil (VGO) distillate (boiling point of around 350–540 °C). In short, 25/75, 50/50, 75/25 %wt. mixtures of bottom residues with VGO were mixed in a 5 mL vial, homogenized and spread in microscope glass slides. Microscope observation was used to identify the presence of precipitates in the mixture.

2.4. Analytical methods

Carbon, hydrogen, nitrogen, sulfur and oxygen (by difference) were determined using combustion analysis (Elementar Vario EL Cube). Analysis were performed according to ASTM D5291 for CHN and DIN 51724-3 for sulfur. To estimate higher heating value (HHV), the Channiwala-Parikh correlation [30] was used (Equation (1)). Carbon and nitrogen balances were calculated according to Equation (2).

$$HHV\left[\frac{MJ}{kg}\right] = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (1)$$

$$\text{Elemental balance}\,\% = \frac{\text{yield}_{\text{phase}}\left[\frac{g_{\text{phase}}}{g_{\text{biocrude}}}\right] . \text{Element content}_{\text{phase}}\left[\frac{g_{\text{Element}}}{g_{\text{phase}}}\right]}{\text{Element content}_{\text{biocrude}}\left[\frac{g_{\text{Element}}}{g_{\text{biocrude}}}\right]} \times 100 \quad (2)$$

Water content in oil phases was measured via coulometric Karl Fischer titration. Density, dynamic and kinetic viscosities were measured using an Anton Paar Stabinger SVM 3000 viscometer at 40 °C. Total acid number (TAN) and basic nitrogen in hydrocarbons were measured using an 888 Titrando (Metrohm). For biocrude TAN, the last turning point among the typically 5 was considered for measurement, while for upgraded products typically only one turning point was observed. Basic nitrogen in hydrocarbons was measured according to UOP method 269-10. Micro carbon residue (μMCR) was determined by Conradson micro method using a Normalab Analysis NMC 420 according to ASTM D4530.

Gas chromatography coupled with mass spectrometry (GC/MS) analysis of biocrudes and hydrotreated products was carried out using an Agilent 7890B GC and a quadrupole mass filter MS Agilent 5977A. Typically, 10 mg of sample was diluted in 1 mL DCM with 4-bromotoluene internal standard. The column used was a VF-5 ms column (65 m × 0.25 mm × 0.25 μm) and the analysis sequence is described elsewhere [31]. Spectra was compared with NIST mass spectra database 2017 for molecular identification.

Simulated distillation was conducted according to ASTM D2887 standard in an Agilent 6890 GC equipped with a capillary column DB-HT-SIMDIS, 55 m × 530-μm id × 0.15-μm and flame ionization detector. Standards and oil samples were diluted in DCM and calculations were performed using Agilent's SIMDIS software.

Group type composition of gasoline was calculated from its individual composition determined by the PONA method, using a Agilent 6890 GC equipped with an FID detector and a capillary column HP-PONA (50 m × 0.2 mm i.d.; film thickness 0.5 μm). Constant head pressure of 140 kPa of nitrogen carrier gas and split 1:100 was applied. The temperature program was following 5 min at 30 °C, then an increase at 2 °C/min to 170 °C.

The content of saturated compounds from kerosene, diesel and bottom residues distillates was determined after separation over a chromatography column filled with $AgNO_3$-SiO_2 (10 g) and Al_2O_3 (4 g). Samples (0.12 g) were dose on the column and saturated fraction was eluted by *n*-pentane (kerosenes and diesels) or *n*-heptane (bottom residues). To allow complete elution of high molecular weight *n*-alkanes, separation of bottom residues was carried out at 80 °C. The amount of saturated compounds was determined by weight after solvent evaporation [32]. After separated, these saturated compounds were diluted in CH_2Cl_2 (20 mg ml^{-1}) and analyzed using an Agilent 7200 GC (oven program starting at 40 °C, 4 min hold, ramping to 300 °C at 10 °C min^{-1} and holding for 5 min with 1.0 mL min^{-1} helium flow as carrier gas) QTOF (EI + 70 eV, scanning 20–600 u at 4 scans s^{-1}). When analyzing kerosenes, a DB5ms column (30 m × 0.25 mm, 0.25 μm film and 1.5 m × 0.15 μm restrictor) was used. As for diesels and bottom residues, a DB-1 ms column (5 m × 0.32 mm, 0.25 μm film and 1.5 m × 0.15 μm restrictor) was used instead. Determination of saturated compounds groups was carried out in agreement with the ASTM D2786 method.

3. Results and discussion

3.1. Hydrotreatment observations

The hydrotreated liquid products were typically composed of a dark oil phase and a clear aqueous phase. Usually, the two phases separated without centrifugation, though the lower the processing temperature the more difficult increased viscosity led to more difficult phase separation. Interestingly, the oil phase collected from manure at 400 °C (400I) had an orange color, clearly differing from all other collected samples (see Figure S4). It was not possible to close the mass balance for 400II in the co-HTL biocrude campaign, thus yields are omitted in the dataset presented in Fig. 1 and Figure S5.

The temperature control for the upgrading campaigns of single-feedstock biocrudes was more stable, as evidenced by lower reactor temperature average standard deviation in Fig. S2AB, compared to the larger deviations for the co-HTL biocrude in Fig. S2C. The increased difficulty in control is also illustrated in Figure S3, where a less even temperature profile over the NiMo bed is shown for co-HTL biocrude upgrading. These observations can be related to the higher complexity of molecules present in co-HTL biocrude, in specific nitrogen-containing heterocyclics [7], known to be more stable and resistant to hydrotreatment. This can cause mass-transfer limitations and prevent other molecules to be hydrotreated with the same kinetics as experienced with single-feedstock HTL biocrudes. The hydrogen consumption for co-HTL biocrude presented in Table S1 corroborates this finding; for co-HTL biocrude the H_2 consumption is generally lower than for the two single-feedstock biocrudes. Hydrogen consumption for the co-HTL biocrude ranges between 11 and 18 $g_{H_2}/kg_{oil\ DB}$, which is much lower than the single feedstock ones (18–36 $g_{H_2}/kg_{oil\ DB}$). These observations (mass transfer limitations) indicate that the use of catalyst extrudates as opposed to the crushed catalysts used in this study could be an additional difficulty for hydrotreatment of co-HTL biocrudes. Such effects of using full extrudates in more realist refinery settings in long-term hydrotreatment operation are still undiscovered and require further development.

Table S2 shows the carbon content of unused and spent catalysts. A lower carbon build-up in the CoMo bed is shown when running the co-HTL biocrude compared to the single-HTL biocrudes. The opposite is observed in the NiMo catalyst bed where more carbon is present for the co-HTL biocrude. This increased carbon layer on the NiMo catalyst particles may have contributed to the mass-transfer limitations and reduced hydrogen consumption involved in the hydrotreatment of the more complex molecules present in the co-HTL biocrude. The carbon contents on catalysts post reaction are nevertheless within expected values based on initial carbon deposition mechanisms [34].

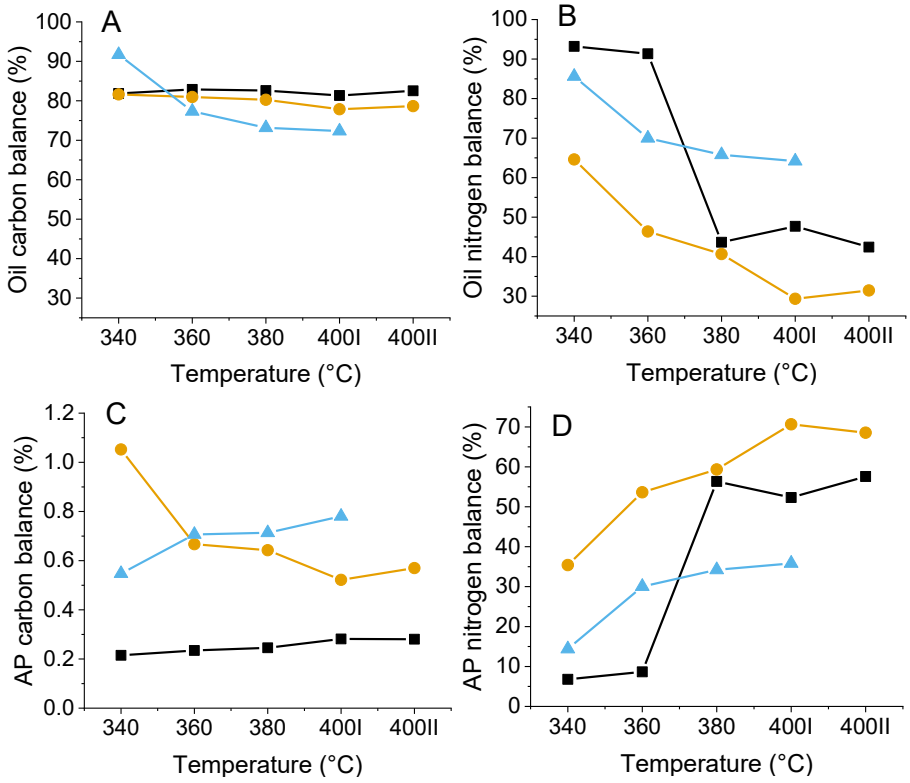


Fig. 1. Carbon (A, C) and Nitrogen (B, D) weight balances to oil (A, B) and aqueous phase (AP) (C, D) over hydrotreatment temperatures tested for wheat straw (WS), cow manure (CM) and co-HTL biocrude (WS + CM).

3.2. Mass, carbon and nitrogen yields

Figure 1A-B shows the effect of hydrotreatment temperature on the oil carbon and nitrogen balances. Additionally, oil mass yields are presented in Figure S5 alongside the AP mass and carbon yields. The upgraded oil yields (Figure S5) ranged from 65 to 85 % and correlate well with lignocellulosic-derived HTL biocrude upgrading with a similar catalyst bed construction [29,33]. The carbon yield to upgraded oil is slightly higher ranging from 75 to 85 %. All carbon balances approached 100 wt% closure within 2 %, and the gas carbon balances are found in Fig. S5C. For biocrudes from single feedstock, the effect of temperature on carbon yield is minimal and the amount of carbon recovered as oil is on average 81 wt%. For the co-HTL biocrude, the effect of temperature on the oil carbon yield is pronounced, dropping from 92 wt% at 340 °C to 73 wt% at 400 °C. Such an effect can be an indication of small sections of carbon (e.g. derived from carboxylic acids, ketones, aldehydes) attached to larger *N*-containing hydrocarbon molecules during the co-HTL process [7], which are released at higher hydrotreatment temperatures, generating more gas (see Fig. S5C) and thus reducing oil carbon recovery. The oil carbon balances are generally higher than lignocellulosic-derived pyrolysis hydrotreated products using similar strategies [11,22], but fall within the range of carbon yields from hydrotreated HTL biocrudes of algae [17,20], sewage sludge [18,20] or lignocellulosic [18] materials. Comparing single feedstock HTL biocrudes to co-HTL bio-crude it can hence be concluded that part of the carbon responsible for generating synergistic effects in HTL processing is promptly released as gaseous hydrocarbons during hydrotreatment, leading to lower oil carbon yields.

Nitrogen balances to oil decreased with increase in temperature at different rates depending on the specific biocrude sample (Fig. 1B). For manure and straw single biocrudes, <50 % of nitrogen remained in the oil at higher temperatures. The co-HTL biocrude on the other hand, showed a less pronounced effect of temperature on the amount of nitrogen recovered in the oil phase, decreasing the amount from 86 % to 64 % within the tested temperatures range. This shows the nitrogen-containing molecules in the co-HTL biocrude are more resistant to hydroprocessing and are more prone to remain in the oil phase, which is supported by the observation of lower hydrogen consumption mentioned above. As these molecules are derived from Maillard-like reactions followed by cyclization [7], these *N*-containing heterocyclic aromatics (both pyridines and pyrroles) stay in the oil phase due to their recalcitrance towards hydrotreatment.

Figure 1C-D depicts the aqueous phase carbon and nitrogen balances. For carbon, yields were in general lower than 1 %, showing that most carbon retrieved from the oil phase ended-up in the gas phase instead of forming water-soluble molecules. The gaseous yield were generally around 18–25 % (see also Fig. S5C), which is in agreement with previous literature [11]. Gases were mostly composed of short chain hydrocarbons and small amounts of CO_2 and CO (Figure S6). Nitrogen mainly yields water-soluble molecules, mostly ammonia, not contributing significant to gaseous products. Generally, with the increase of temperature, lower concentrations of methane are found together with an increase of longer chain hydrocarbons, as *C*2-C7 alkanes. This is related to the increase of cracking reactions, which lead to formation of *C*2-C5 hydrocarbons. It should also be noted around 5–10 % of hydrocarbons found in the gas phase would in practice be recovered in the gasoline fraction given their boiling points. Interestingly, CO and CO_2 were not found in significant concentrations for manure biocrude upgrading. This can be connected to manure's characteristic lower amounts of cellulose in feedstock because of animal digestion of lignocellulosic feed. Such effect leads to a biocrude with almost half the amount of carbonyls groups to be released from manure, in comparison to straw biocrude. The carbonyls content determined by ASTM E3146 was 4.2; 2.2 and 2.8 mmol of carbonyl groups per gram for straw, manure and co-HTL biocrude.

Table S1 shows the elemental composition of biocrudes and their respective hydrotreated products. The hydrotreatment process is successful in deoxygenating (>90 %) all biocrudes at temperatures of and

above 360 °C, reaching 100 % in all samples at 400 °C, however denitrogenation is not as successful. As shown in Fig. 1B, the co-HTL biocrude exhibits more nitrogen in the hydrotreated oil when compared to single-feedstock biocrudes. The denitrogenation of the single-feedstock biocrudes is significantly higher than the combined one. Between the two single feedstock biocrudes, the manure biocrude shows highest denitrogenation. This is connected to nitrogen coming from proteins in manure, which has higher reactivity towards hydrogen than the heteroaromatics found in both straw and co-HTL biocrude. This effect illustrates further how the same molecules that generate HTL synergies impact hydrotreatment negatively with regard of nitrogen removal.

3.3. Hydrotreatment products physicochemical characteristics

Fig. 2 depicts physicochemical characteristics of biocrudes and oil from hydrotreated products. Kinematic viscosities decreased significantly, from 1300 to 5000 $mm^2.s^{-1}$ for the biocrudes (where the co-HTL biocrude was the most viscous), to 2–14 $mm^2.s^{-1}$ for hydrotreated products at 400 °C (Fig. 2A). Increasing the temperature from 340 °C to 400 °C decreased viscosity values one to two orders of magnitude, illustrating that deoxygenation significantly impacts viscosities in such biocrudes. Fig. 2B shows the density decrease from biocrudes (>1.05 $g.cm^{-3}$) to hydrotreated oil products (down to 0.85 $g.cm^{-3}$), where the lowest density in all temperatures tested was observed for cow manure biocrudes. The characteristics of all hydrotreated products prepared at 400 °C are comparable to the ones from sewage sludge and food waste HTL biocrude in terms of viscosity and density [26].

The water content decreased to values under 1 wt% (Fig. 2C) for all hydrotreated products, showing that even at 340 °C a significant decrease in polarity was achieved. This is in line with the previously commented enhancement in phase separation, relative high deoxygenation (Table S1) and is comparable to hydrotreated products previously reported in literature [20]. Fig. 2D-H depict that the micro carbon residue (MCR) and TAN were decreased significantly after upgrading. The high temperature upgraded samples exhibit only slightly higher MCR and TAN values than some heavy crude oil types, showing that further refining of these oils would not require major modifications to current refinery reactor material construction [35]. A TAN lower than 1 mg_{KOH}/g has been shown to decrease corrosion, enhancing material durability in long term operation of refining processes using such upgraded products [35]. Simultaneously, a low carbon residue is desired for liquid fuels and the decrease from ~26 wt% to <5 wt% depicts that hydrotreatment was successful in eliminating most coke-prone structures present in biocrude. Even so, there is a sensible increase in MCR with temperature for the co-HTL biocrude upgraded products, which can be related to *N*-containing aromatics leading to cocking structures. Nevertheless, such MCR values are considered acceptable for bunker fuel applications [36] and should not be a challenge if further refining processing is required.

The fraction of basic nitrogen species of the total nitrogen content

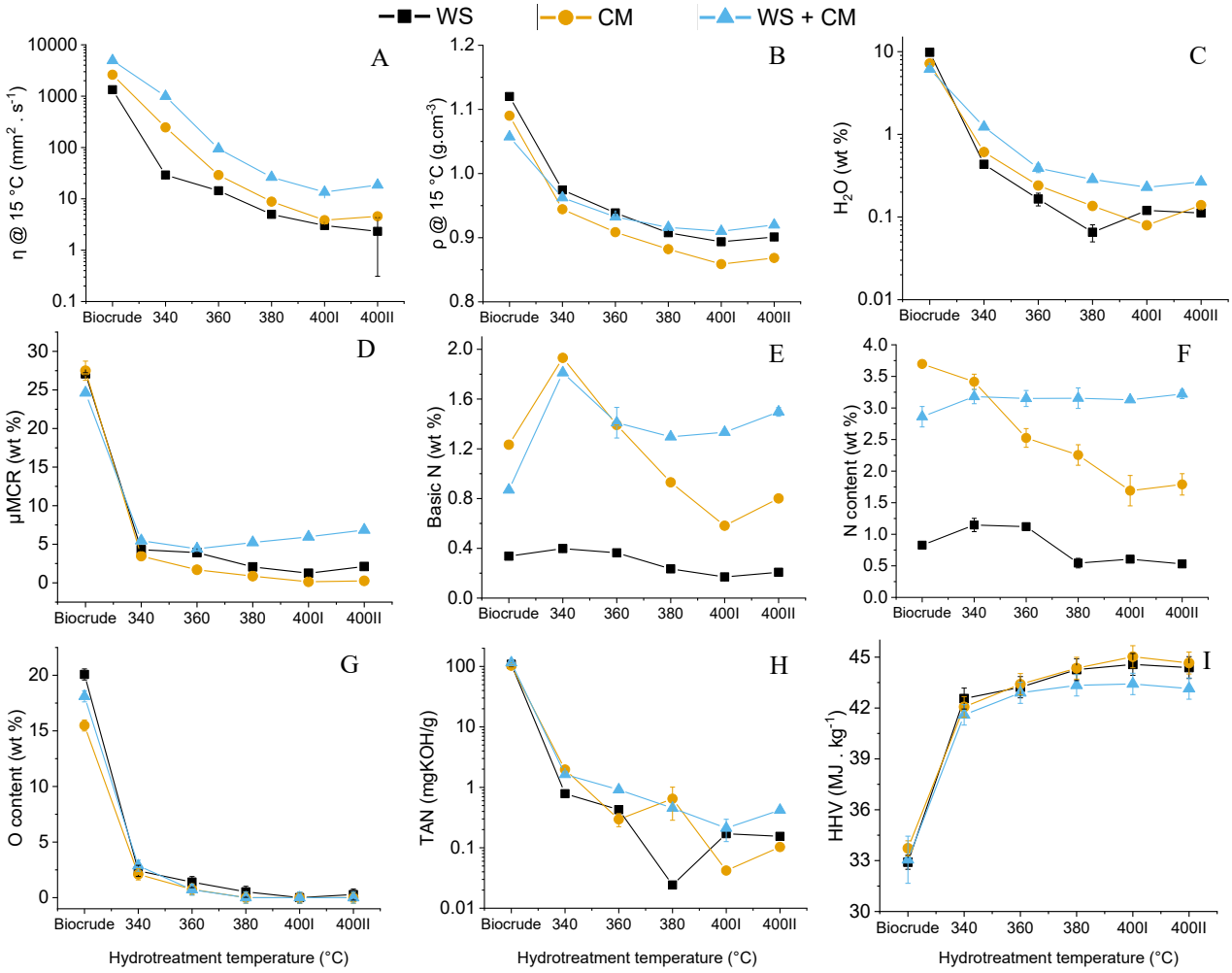


Fig. 2. Kinematic viscosity (η) (A); density (ρ) (B); water content (C); micro carbon residue (μMCR) (D); basic nitrogen in hydrocarbons (E); nitrogen content (F); oxygen content, dry basis (G); Total Acid Number (TAN) (H) and; high heating value (HHV) (I) of wheat straw (WS), cow manure (CM) and co-HTL biocrudes (WS + CM) followed by respective hydrotreated oil products at different temperatures.

(Fig. S7A) in biocrudes is around 30–41 %, the lowest being for the co-HTL biocrude, the highest for wheat straw. For the hydrotreated products, this fraction is higher for the low temperatures, reaching 56 % for cow manure and the co-HTL biocrude. With an increase in temperature, this fraction decreases, reaching 28–42 %, where the highest is for the combined biocrude and the lowest the wheat straw derived oil. The increase in basic nitrogen fraction from biocrudes to low temperature hydrotreated products depicts that the non-basic N compounds are more easily hydrotreated. On the other hand, with the increase in temperature there is a decrease in basic nitrogen fraction, showing that more severe conditions make basic nitrogen species as prone to hydrotreating as non-basic ones. Thus, at least part of the basic and non-basic nitrogen species contained in all biocrudes are recalcitrant during hydrotreatment, however, it seems the co-HTL oil maintains the highest fraction of basic nitrogen of the total nitrogen (Fig. 2E-F). This means the basic nitrogen species of the co-HTL biocrude are less reactive, correlating well with expected larger molecules containing nitrogen in this biocrude [7] and a μMCR increase with temperature during hydrotreatment. So, the larger the nitrogen-containing molecule, the less prone it is to hydrotreatment due to aromatic stability and more prone to cocking reactions.

Fig. 1B shows a larger yield of nitrogen of co-HTL biocrude than the one for single feedstock biocrudes. Interestingly, only the nitrogen content of co-HTL derived hydrotreated oil does not change with temperatures. Such an effect can be associated with more complex molecules containing nitrogen in the co-HTL sample, as discussed in the previous study that described the biocrude production [7]. I.e. the basic nitrogen in the manure biocrude is mostly comprised of amines, prone for easier hydrotreatment, while for the co-HTL biocrude pyridines are likely the basic N compounds present, which being aromatic are more difficult to undergo hydrodenitrogenation. Thus, the manure hydrotreated products' decrease in basic N and N content illustrates that the co-HTL biocrude N compounds require a more aggressive approach for total denitrogenation. All hydrotreated products have HHVs higher than 42 $MJ.kg^{-1}$ (Fig. 2I), but only single feedstock biocrudes reach >44 $MJ.kg^{-1}$ values for high temperature hydrotreated samples, given the negative contribution of nitrogen content to HHV (Equation (2)) and the co-HTL biocrude products N content.

As already reported by PNNL's upgrading research team [26], there is a high correlation between nitrogen contents and density of upgraded products. We report here the same observation (Fig. S7B), though the correlation is feedstock-dependent and cannot be verified for the combined biocrude, as its nitrogen content did not change significantly.

The combined HTL biocrude showed slightly inferior physicochemical characteristics among the ones measured here. Its most distinguishing characteristic is the nitrogen content, which seems to be in forms of recalcitrant molecules towards hydrotreatment. This could affect severely the application of combined feedstock in HTL setups, however the gain in carbon recovery is a major factor to be considered, as described below.

In general, the increase in temperature increased also the hydrotreated product quality in terms of its physicochemical properties. Remarkably, dynamic viscosity, density, water content, MCR, TAN, oxygen concentration (dry basis) and HHV reach numbers close to crude oil specifications, which is a prerequisite for direct refining. Despite that, the nitrogen contents for manure and co-HTL derived products are a challenge to address before direct application as fuels and entails further processing. Even bunker fuels are expected to have a lower nitrogen content than the ones found in these upgraded products. Nevertheless, as depicted in the case of straw-derived upgraded products, the characteristics of these upgraded products are close to bunker fuel specifications [36] and may be an opportunity for its use without further refining.

The straw derived products have similar nitrogen contents to crude oils with high amounts of this element, depicting a similar scenario as other HTL hydrotreated biocrudes from lignocellulosic materials [37,38]. As described elsewhere [20], lower WHSV (around 0.1 h^{-1}) can achieve enhanced denitrogenation of biocrudes with similar initial N content using similar catalyst strategies as we described here, however typical hydrotreatment processes in crude oil refinery use much higher WHSV (0.7–12 h^{-1}) [12]. Thus, given the results shown here, it is likely that such HTL biocrudes would need specific units in refining setups to reach deep denitrogenation, even though deoxygenation and reasonable physicochemical properties are achieved with 0.5 h^{-1} WHSV. As the nitrogen content can be related to specific molecular weights present in these hydrotreated products, a following distillation step can assist on decreasing the contents and concentrating those in more specific and less volumetric byproducts.

It is nevertheless important to consider the final application of the hydrocarbons produced using the strategy depicted in this study. Even deep denitrogenation strategies using HTL biocrudes [20] may not reach nitrogen levels required for sustainable aviation fuels (<2 mg/kg) [39]. However, heavy-duty transportation for example may be able to tolerate nitrogen presence and still fulfil emission requirements [40].

3.4. GC/MS of hydrotreated products

GC/MS total ion chromatograms are shown in Fig. 3A-C normalized to highest ion count. Only the sample volatile and semivolatile fractions eluted can be analyzed, however it is still possible to see the classic biocrude components [41] for lignocellulosic feedstock materials, such as substituted phenolics, ketones, alcohols and nitrogen-containing small heterocyclics. As for the upgraded products, a range of C4-C18 hydrocarbons are observed. Among those, cyclics, aromatics, alkanes and alkenes. The deoxygenation was particularly efficient for this fraction and it was not possible to identify oxygenated compounds in the upgraded samples. These results are in good agreement with the Van Krevelen diagram in Figure S8.

The main difference between upgraded products was the relative presence of long linear chain hydrocarbons derived from lipids in comparison to branched C4-C9 hydrocarbons. The C12-C18 class compounds increased from straw, manure and combined upgraded products respectively. These results can indicate that either the combined approach increased their concentration by converting also straw derived carbon into long chain alkanes or that the amount of small branched hydrocarbons decreased in comparison to the lipid-derived class. According to results of simulated distillation and distillates physicochemical characteristics to be discussed in the following section, this is due to a decrease in light hydrocarbons.

The light hydrocarbons (C4-C10) identified in the hydrotreated samples are all compatible gasoline-range hydrocarbons and have similar H/C ratios to the ones identified in the experimental distillate sample Van Krevelen diagram (Figure S8). This corroborates further the quality of the gasoline fraction derived from all hydrotreated biocrudes, suggesting that addition of this fraction to crude-oil derived gasoline can be an option for its application.

3.5. Distillation of hydrotreated products

Gasoline, kerosene, diesel and bottom residue (BR) distillation cuts are shown in Fig. 4A-D. Experimental distillation cuts were determined within ±3.5 % for all 400 °C hydrotreated products simulated distillation. Thus, simulated distillation values will be considered for further discussion on the effect of temperature on the distillate cut yields. For the experimental distillation cuts, all gasoline and kerosene fractions were transparent upon immediate recovery, while diesel cuts had a light yellow color and BRs had dark and viscous appearance. The highest experimental distillation cut was the BR for straw and co-HTL upgraded products, while for manure biocrude upgraded products, it was the diesel fraction. This is related to the relative higher amount of lipids in manure in comparison to the other feedstocks. Lipids tend to lead to the formation of carbon chain lengths compatible with diesel specifications [7].

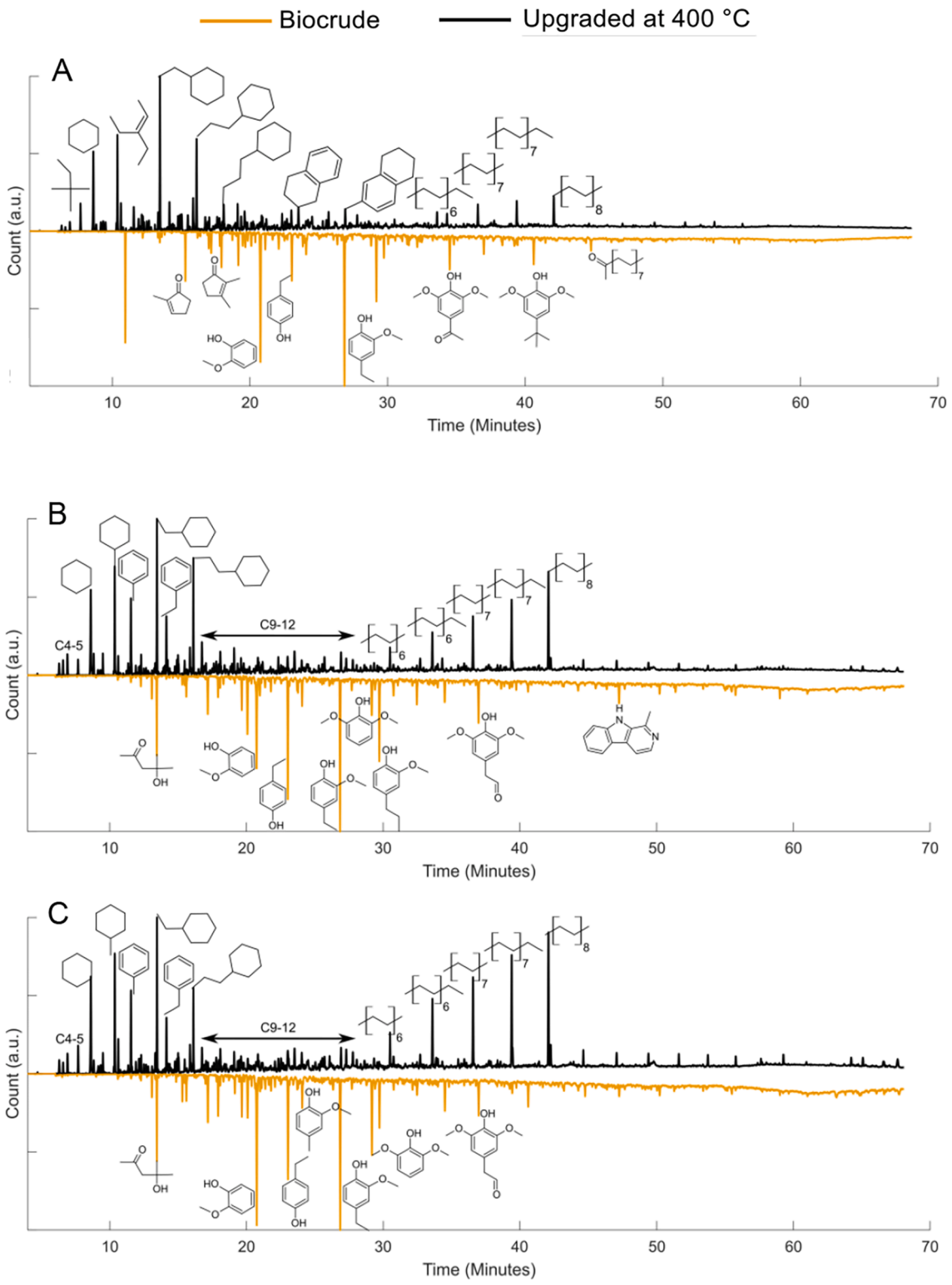


Fig. 3. GC/MS of biocrudes and hydrotreated products (400 °C). (A) Wheat straw; (B) Cow manure; (C) co-HTL biocrude.

In Fig. 4A it is shown that for straw biocrude upgrading, the increase of hydrotreating temperature from 340 to 400 °C resulted in a 3.6 wt% gain in gasoline yield, while for manure and co-HTL biocrudes, the gain was 13.5 and 10.7 wt% respectively. The highest gasoline yield observed experimentally was for manure biocrude hydrotreatment (20.7 %). The results presented for gasoline yields are around 1 to 2 wt% less than expected in practice, given their composition and the compounds identified in the gas phase which would typically contribute to gasoline as discussed in section 3.2. Fig. 4B shows that the hydrotreatment temperature increased the kerosene yields from 17.2, 17.4 and 15.6 wt% at 340 °C to 24.1, 22.2, and 18.6 wt% at 400 °C for straw, manure and co-HTL biocrudes, respectively. This means the temperature effect on the increase of this cut was higher for single feedstock biocrudes than for the combined one. The highest experimental kerosene yield observed was for straw with 23.7 wt%.

The diesel distillation cuts shown in Fig. 4C only depict an increase of

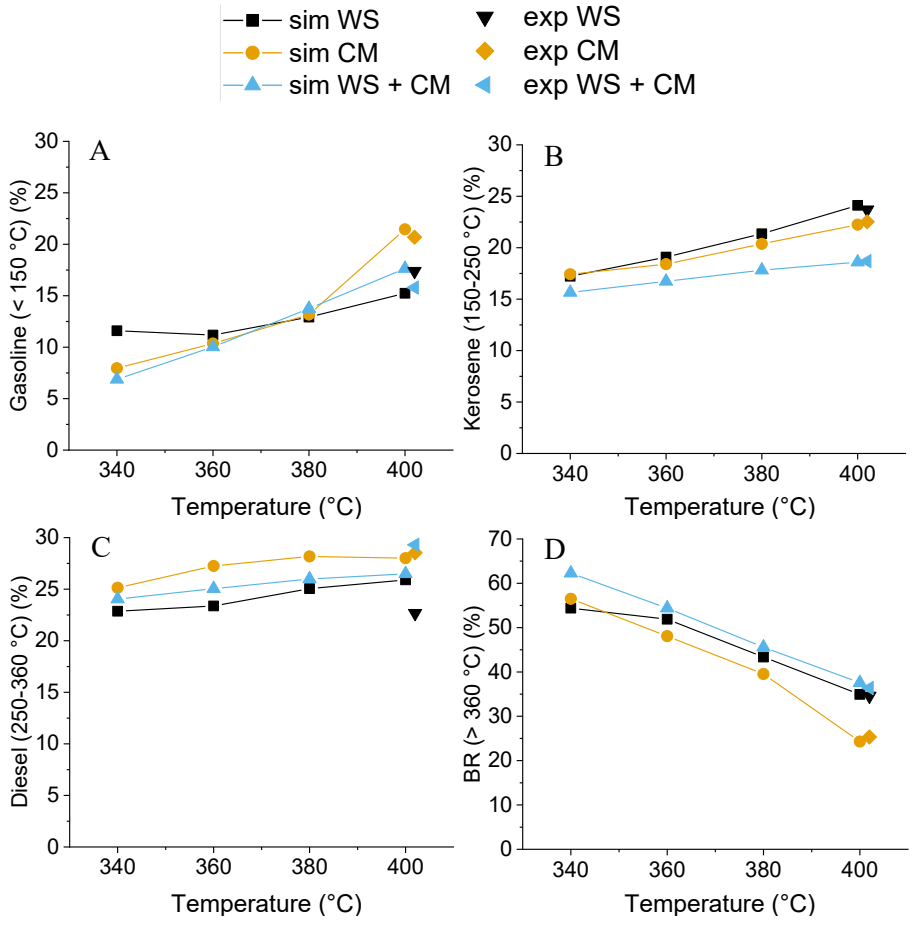
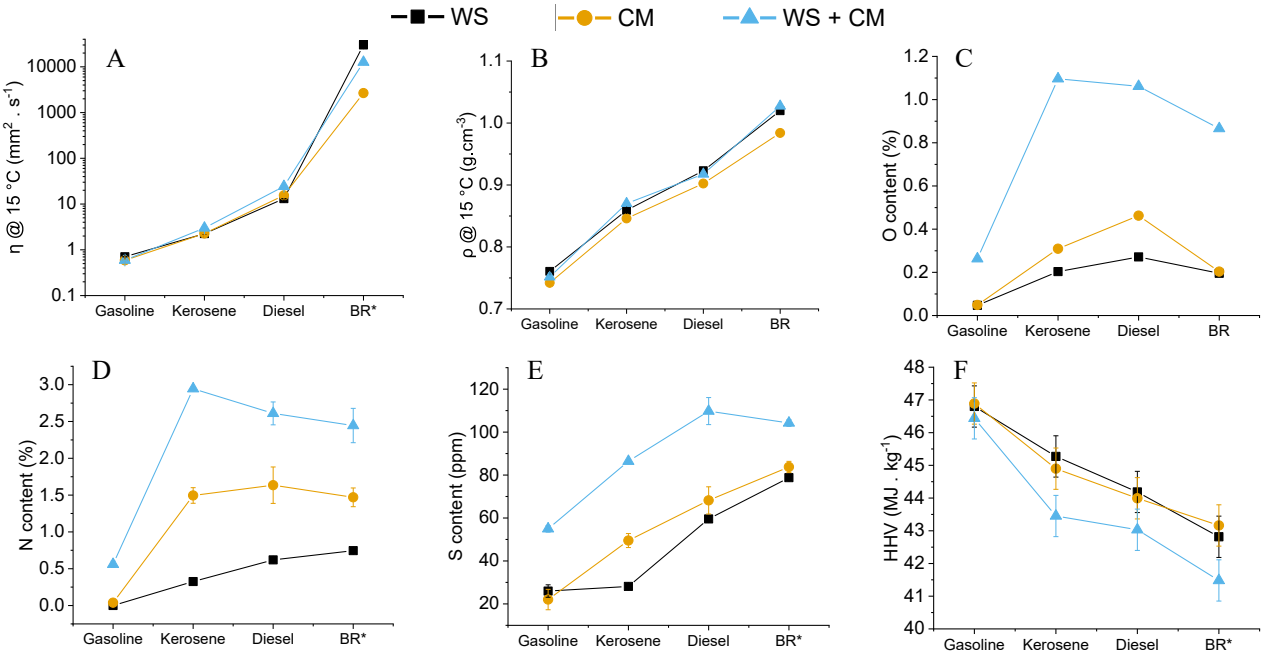


Fig. 4. Simulated and experimental distillation cuts (wt%) for gasoline (A), kerosene (B), diesel (C) and bottom residue (BR) (D) for all hydrotreated products. (sim – simulated distillation GC analysis for all hydrotreated products at different temperatures; exp – experimental distillation yields for hydrotreated products at 400 °C; WS – wheat straw; CM – cow manure; WS + CM – co-HTL biocrude).



* - BR = Bottom Residue; viscosities of WS + CM BR were measured at 50 °C due to equipment limitations

Fig. 5. Dynamic viscosity (μ) (A); density (ρ) (B); oxygen content by difference, dry basis (C); nitrogen content (D); sulfur content (E) and; higher heating value (HHV) (F) of distilled products from hydrotreatment at 400 °C of biocrudes from wheat straw (WS), cow manure (CM) and co-HTL biocrude (WS + CM).

around 3 wt% with increasing temperature for all biocrudes. No significant change was observed in all upgraded products with an increase of 380 to 400 °C in hydrotreating temperature. However, Fig. 4D depicts that there is a substantial decrease of bottom residue (BR) with the increased temperature. The yields of this fraction decrease from 54.4, 56.5 and 62.3 wt% at 340 °C to 34.9, 24.3 and 37.6 wt% at 400 °C, respectively for straw, manure and co-HTL biocrude products. The decrease in BR is highest for manure biocrude, though on average there is an 8.5 ± 1.1 wt% decrease in BR yield for every 20 °C increase in hydrotreatment temperature. This observation shows that the increase in hydrotreating temperature decreases BR components, which is corroborated by the increase of gasoline and kerosene fractions. Surprisingly, the diesel fraction did not change significantly, which suggests that either the components consumed from BR are transferred directly to kerosene and gasoline or that the increase in temperature also increased cracking reactions in the diesel fraction, which equilibrates material gain from the BR. Nevertheless, increasing temperature clearly increased light hydrocarbons yields, benefiting mostly gasoline for manure and co-HTL biocrude and kerosene for straw.

Figure 5A-F depicts physicochemical characteristics of the 400 °C hydrotreated biocrudes distilled fractions. Density and viscosity (Fig. 5A-B) of gasoline, kerosene and diesel fractions are similar among the different hydrotreated products. However the BR viscosity of the combined biocrude is much higher, to the point it was not possible to measure it at 40 °C, so values are shown at 50 °C. These viscosities are one order of magnitude apart, where manure, straw and co-HTL are ordered from lowest to highest viscosity and density. The gasoline nitrogen content was almost zero for straw and manure, for the combined biocrude however it reached 0.5 wt% (Fig. 5D). For straw, the heavier the fraction, the higher the nitrogen content. For manure, nitrogen contents of kerosene, diesel and BR were around 1.5 wt%. As for the combined biocrude products, kerosene had the highest nitrogen content with almost 3.0 wt%, while diesel and BR from this fraction presented 2.5 wt%. Thus, the nitrogen containing molecules tend not to be present in the gasoline, showing that the smaller the molecule, the more prone it is for denitrogenation. These findings open up the possibility for heavier fractions to be further refined in specific processes targeting nitrogen containing molecules.

The S content of distillates was between 20 and 110 ppm (Fig. 5E), which is higher than current fuel standards and highlights the need of further upgrading or blending with low S content alternatives. The S content for the co-HTL upgraded distilled products in particular seem consistently higher than others, ranging from gasoline at 52 ppm to diesel at 108 ppm. HHV of distillates depicted in Fig. 5F reduce for the heavier fractions and are higher for the single-HTL distillates than the co-HTL. This is derived from the higher nitrogen content and unsaturated compounds of the latter (see also Figure S8 where lower H/C ratios point to increase of aromatics and unsaturated compounds). Nevertheless, HHVs are relatively high and within fuel standards.

The Van Krevelen diagram of all biocrudes, upgraded and distilled samples (Figure S8 A-D) showed that biocrudes O/C ratio were around 0.25–0.35, typical values, while the upgraded products were all <0.03. Even though O/C ratios are that low, there is still a trend for the higher the temperature, the lower the O/C ratio. H/C values for upgraded products were around 1.6–1.8, while the distillates have clear separation for gasoline, kerosene, diesel and BR showing H/C ranges of >2.0, 1.75–1.80, 1.60–1.65 and 1.25–1.45 respectively. Gasoline and kerosene samples are generally within crude oil derived H/C and O/C limits, however diesel presents a lower H/C. This indicates gasoline H/C values are compatible with C6-C15 alkanes, as for kerosene, diesel and BR alkenes, unsaturated cyclic hydrocarbons and polyaromatics H/C ratios are more likely to be present in high concentrations. A lesser content of alkanes in heavier fractions decreases H/C values and is in agreement with the type of catalyst used, selected based on deoxygenation potential rather than saturation [11]. Still, the observation highlights the lighter the molecules, the more prone they are to be deoxygenated, denitrogenated and saturated via hydrotreatment.

The gasoline distillation product was mostly composed of cycloalkanes for all feedstock biocrudes processed (Fig. 6), even though CoMo and NiMo catalysts are typically used due to their deoxygenation activity. While straw generated more cycloalkanes than the other two biocrudes, *n*-alkanes were present in higher quantities in manure products. This is related to a higher amount of lipids in these feedstock materials, leading to *n*-alkane formation during hydrotreatment. Aromatics compose 7.7 wt% for straw products and 10.4 wt% for both manure and co-HTL biocrude hydrotreatment products. The typical higher amount of lignin in manure lignocellulosic components can be connected with the difference for single-feedstock biocrudes. While for the co-HTL biocrude, a higher amount of aromatics in the biocrude [7] also yields higher amounts of aromatics in the gasoline distillation cut. The isoalkane concentration in co-HTL oil was the average of that of both single-feedstock biocrude upgraded products. This compound class was likely derived from molecules not involved in the synergistic effects of co-HTL, which may be short chain ketones and aldehydes [7]. Due to the high abundance of cycloalkanes, the calculated octane number for straw, manure and co-HTL biocrude hydrotreated products were 63, 61 and 64, respectively. This much lower octane number than the 95 of fuel-grade petrol (BS EN 228:2008) shows the need of further treatment via isomerization and reforming, even though limits (BS EN 228:2008) for olefin (<18 vol%), aromatics (<35 vol%), benzene (<1.0 vol%), oxygen (<2.7 wt% dry basis) are all met.

Figure 7A-C depicts that the lighter the distillate fraction, generally the higher the saturated composition by weight for each different feedstock biocrude. An exception was the cow manure product, which contained similar amounts of saturated compounds both in the kerosene and diesel fractions.

Out of all kerosene fractions produced, the straw-derived product had the highest amount of saturated compounds (Fig. 7A). This increased amount is connected to the relatively higher presence of monocycloparaffins and dicycloparaffins in the straw product when compared to the different kerosenes. For diesels (Fig. 7B), both straw and manure diesel fractions contained very similar amounts of saturated compounds, despite a higher presence of *n*-alkanes and isoalkanes in the manure diesel. This can be connected to a higher presence of lipid-derived molecules in the manure biocrude when compared to the straw one [7]. As for bottom residues (Fig. 7C), saturated compounds only accounted for 15 to 26 wt% of the samples, the highest being for cow manure, due a higher presence of tetracycloparaffins.

In general, the co-HTL products presented lower amounts of saturated compounds in all distillate fractions analyzed, including gasoline. This observation is compatible with the discussions already described

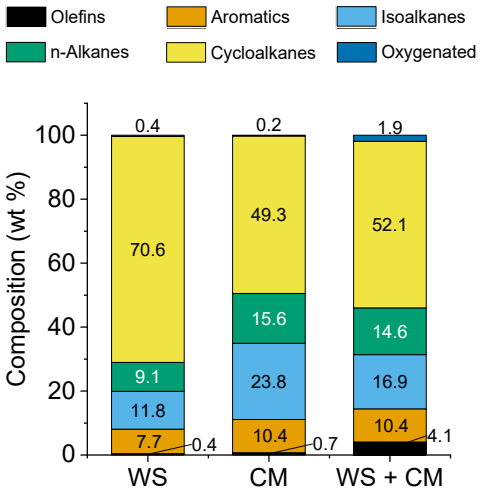


Fig. 6. Composition analysis of distilled gasoline fraction (<150 °C).

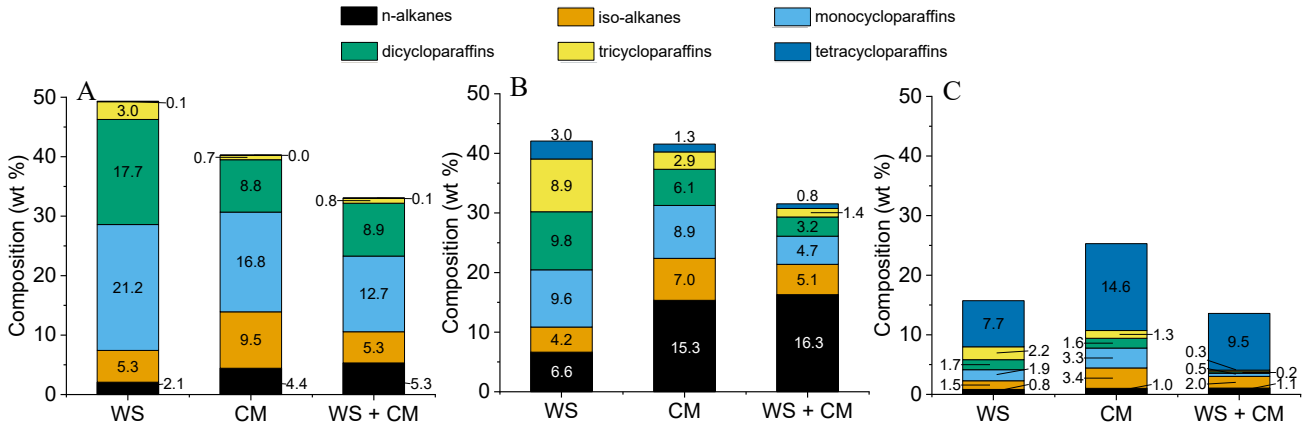


Fig. 7. Composition analysis of the saturated compounds in distilled kerosene (150–250 °C) (A), diesel (250–360 °C) (B) and bottom residue (>360 °C) (C) fractions. WS = wheat straw; CM = cow manure; WS + CM.

here regarding nitrogen-containing aromatics and their nature in the co-HTL product. In practice, these molecules prevent the full denitrogenation and hydrogenation required for saturated compounds to be formed from biocrudes.

The solubility of all bottom residue fractions in vacuum gas oil distillate (boiling points of around 350–540 °C) was tested. The selected crude oil fraction is representative of a common hydrocracking unit feed. Bottom residues from single feedstock biocrudes did not present phase separation at room temperature. The co-HTL derived bottom residue fraction presented two phases in the form of a suspension in presence of all ratios of VGO tested. Increasing the temperature to 45 °C eliminated the biphasic separation for the mixture containing 75 % of bottom residue, showing that an increase in temperature can be effective in enhancing the miscibility. Thus, co-processing via hydrocracking of the BR distillate product with fossil VGO can be considered as a possible approach to increase biofuel light hydrocarbon yields.

3.6. Process carbon balance

In order to compare the benefits and drawbacks of combined processing of manure and straw via HTL followed by hydrotreatment at 400 °C and product distillation, a carbon balance of the entire approach – 1000 kg of carbon biomass to biofuels – is shown in Fig. 8A-C. The results for HTL have already been published elsewhere [7]. The most significant carbon loss for all approaches is in the HTL-derived aqueous phase, ranging from 365 kg for wheat straw to 392 kg for manure. The combined approach yields 369 kg of carbon in this fraction. Treatment of aqueous phase compounds can be considered a resource rather than waste handling [42], when gasification [42], wet oxidation [43] or electro-oxidation [44] technologies are applied. Thus, this aqueous phase carbon is not necessarily a carbon loss, depending on the approach to be considered.

Solids from HTL carry around 100 kg of carbon from single feedstock processing, however this number was reduced to 56 kg in the combined approach. The solids from HTL of agricultural waste streams are rich in phosphorus [45], and further processing is needed to retrieve fertilizer-grade forms of this element [46]. Thus, the reduction of carbon yielded as solids in the HTL process can also be beneficial for the handling and valorization of this fraction, greatly benefiting agricultural management of land and soil nutrient circularity.

For every 1000 kg of carbon entering a HTL unit in the form of wheat straw, manure or a combination of both, 410, 440 and 531 kg of carbon ended-up as biocrude respectively. If the process was non-synergistic, the combination of feedstock materials would result in 425 kg, as oppose to the experimental 531 kg, which represents a 25 % gain. In the hydrotreatment step, the combined HTL biocrude yields a greater gas fraction, leading 100 kg of carbon to this byproduct, though still maintaining a larger overall efficiency by generating 427 kg of carbon as upgraded oil as opposed to 338 or 380 kg of carbon for single feedstock approaches. That is, despite losing more carbon in the gas fraction, the combined HTL approach still achieves a greater carbon efficiency for upgraded oils (almost 43 %). Overall, light hydrocarbons (boiling points <360 °C) have a total carbon yield from feedstock of 21.6, 27.2 and 26.5 % respectively from wheat straw, cow manure and the combined biocrude. That is, the co-HTL approach does not enhance carbon yields compared to pure manure, however it does act synergistically towards the production of light hydrocarbons.

The distillation step illustrates further benefits and drawbacks of combining waste materials in the HTL process. On one hand, gasoline and kerosene did not gain much in terms of carbon yield using co-HTL. On the other hand, it seems the gain in upgraded oil carbon was entirely transferred to diesel and bottom residues, which increase to 121 kg and 152 kg of carbon versus 77–108 and 117–96 kg for single feedstock straw and manure, respectively. The increase in BR production highlights the need of further hydrocracking of this fraction to yield light distillates. The miscibility of BR and VGO can ease processing of these highly viscous products.

4. Conclusion

From a broad processing perspective, the co-HTL of agricultural wastes can increase the amount of hydrocarbons produced through hydrotreatment, achieving a higher carbon efficiency from biomass to hydrocarbon products. However, the denitrogenation required to produce fossil-grade hydrocarbons through hydrotreating are hindered by the presence of the same compounds that generated synergy gains in HTL. Thus, a more aggressive approach targeting specifically these compounds has to be considered as a further refining step if lower nitrogen contents are necessary.

All hydrotreated products obtained through the route proposed here using typical industrial catalysts have attractive physicochemical characteristics and appear suitable to modern refining facilities and equipment. Low TAN, oxygen content, viscosities, density and MCR, together with crude-like HHV corroborates this statement. The upgraded products have characteristics comparable to marine bunker fuels, which should be an option to consider given that ship engines accept higher nitrogen concentrations.

The distillates after hydrotreatment show good correlation to biofuel specifications, meaning the chosen upgrading strategy significantly enhances bio-liquid quality and increases value. All heavy fractions obtained through distillation show good solubility in fossil-derived VGO, which opens possibilities in combined processing of those in current

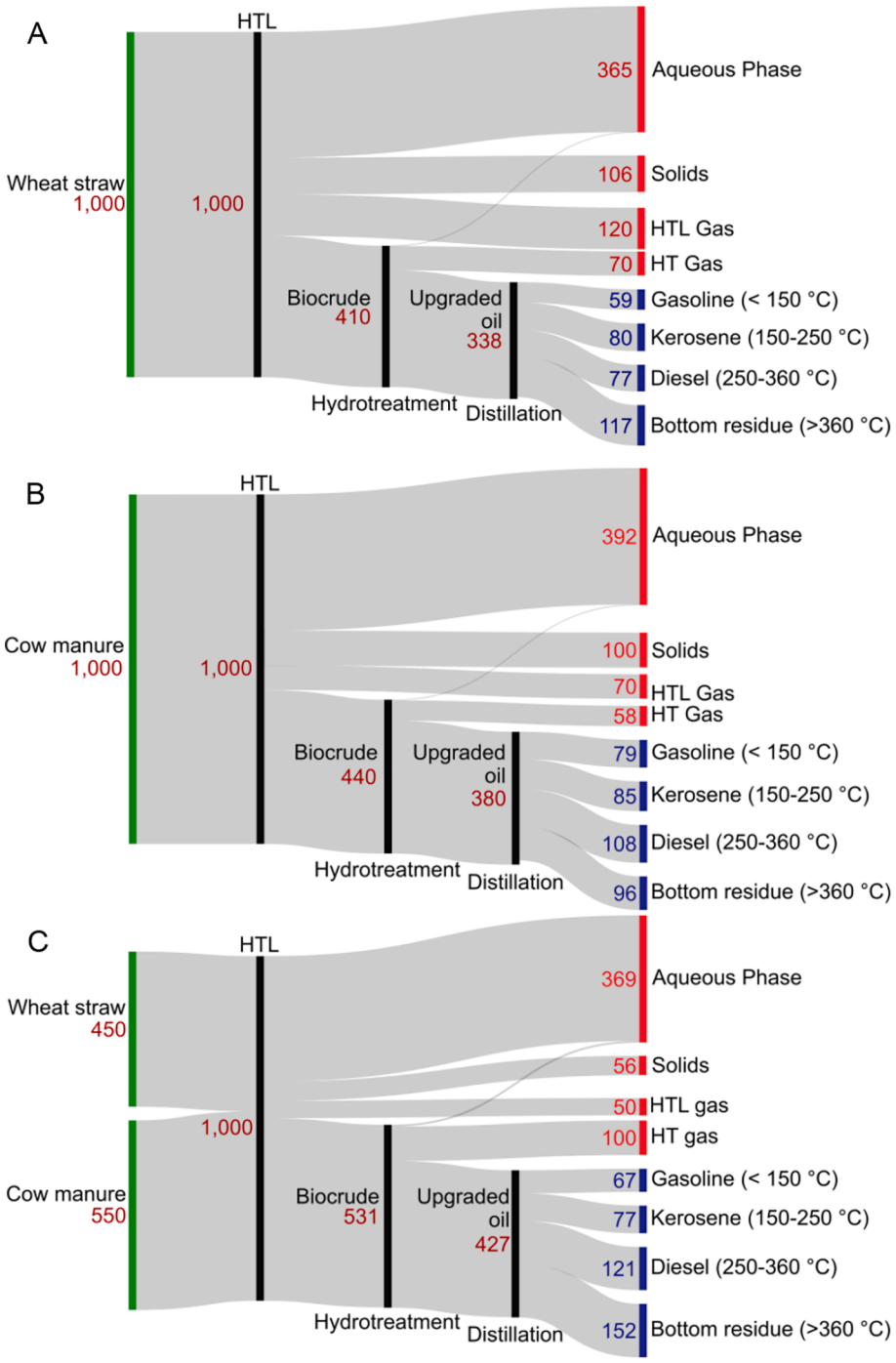


Fig. 8. HTL, hydrotreatment and distillation total carbon balance for all three feedstock slurries starting with 1000 kg of carbon. (A) Wheat straw; (B) Cow manure; (C) combined wheat straw and cow manure.

refinery infrastructure.

There is still a need for developing improved approaches for dealing with nitrogen-containing recalcitrant molecules and isomerization for biofuel applications in small engines. The combination of agribusiness waste for co-HTL processing is shown to be an attractive solution for wet waste processing and enhanced carbon recovery towards advanced biofuels from 34 to 38 % to 43 %.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.139636.

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